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			5c. PROGRAM ELEMENT NUMBER 611103		
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			5e. TASK NUMBER		
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14. ABSTRACT Funds were used to purchase a Renishaw inVia Reflex Spectrometer System for Raman and Photoluminescence spectral analysis of thin film coatings, bulk materials, powders and nanoparticles. The instrument is extensively used to characterize advanced electrochemical and electronic materials. The instrument is equipped with a confocal microscope, two lasers for excitation at different wavelengths, a movable stage and optics for spatial imaging, a temperature-controlled sample compartment, and photoluminescence imaging. The instrument is used by undergraduate and graduate students as well as faculty from across the MSU campus who are engaged in the					
15. SUBJECT TERMS Raman spectroscopy, Photoluminescence measurements					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Greg Swain
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 517-355-9715

## Report Title

Final Report: Purchase of a Raman and Photoluminescence Imaging System for Characterization of Advanced Electrochemical and Electronic Materials

### ABSTRACT

Funds were used to purchase a Renishaw inVia Reflex Spectrometer System for Raman and Photoluminescence spectral analysis of thin film coatings, bulk materials, powders and nanoparticles. The instrument is extensively used to characterize advanced electrochemical and electronic materials. The instrument is equipped with a confocal microscope, two lasers for excitation at different wavelengths, a movable stage and optics for spatial imaging, a temperature-controlled sample compartment, and photoluminescence imaging. The instrument is used by undergraduate and graduate students as well as faculty from across the MSU campus who are engaged in the characterization and study of new and emerging materials. This Renishaw system is a powerful material characterization tool that provides exquisite morphological, elemental and electronic property (dopant distribution) information spatially across a material (surface and bulk). The instrument supports advanced interdisciplinary research (chemistry, materials science, electronics and physics) in the department and across campus, and is aiding in our understanding of new materials and molecular interfaces, interfacial electron-transfer processes, electrocatalysis, electronic properties of materials, and the physical and chemical properties of inorganic quantum dots. Several ongoing research projects are greatly benefiting from the new instrument. Some of the project accomplishments during the past year are highlighted below.

In addition to benefiting materials research, we are using the instrument in a new experimental module on material characterization for CEM 435 Advanced Analytical Chemistry/Instrumental Analysis (20-30 undergraduate students per year).

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**Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:**

**(a) Papers published in peer-reviewed journals (N/A for none)**

<u>Received</u>	<u>Paper</u>
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**TOTAL:**

**Number of Papers published in peer-reviewed journals:**

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**(b) Papers published in non-peer-reviewed journals (N/A for none)**

<u>Received</u>	<u>Paper</u>
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**TOTAL:**

Number of Papers published in non peer-reviewed journals:

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(c) Presentations

Some of these preliminary results were presented by Rémi Beaulac during the 249th ACS meeting in Denver, in March 2015, in a presentation titled: “New Approach to the Synthesis of Quantum Confined Nitride Nanoparticles”.

Corrosion Inhibition of TCP-Coated AA2024-T3 during Exposure to SO2 Atmospheric Testing by Greg Swain, Liangliang Li, Brandon Whitman, presented at the Spring Electrochemical Society Meeting, Chicago, IL, May 2015, Abstract #1092.

The Role of Chromium (III) in the Corrosion Inhibition of AA2024-T3 By Trivalent Chromium Process Coatings by Greg Swain, Brandon Whitman, presented at the Spring Electrochemical Society Meeting, Chicago, IL, May 2015, Abstract #1093.

Number of Presentations: 3.00

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Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

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(d) Manuscripts

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Manuscripts:

Books

Received      Book

TOTAL:

Received      Book Chapter

TOTAL:

Patents Submitted

None

Patents Awarded

None

Awards

None

Graduate Students

NAME	PERCENT SUPPORTED	Discipline
Andre Castiaux	0.00	
Catherine Munson	0.00	
Brandon Whitman	0.00	
Matthias Muehle	0.00	
Dan Little	0.00	
Tung-Wu Hsieh	0.00	
Omid Zandi	0.00	
FTE Equivalent:	0.00	
Total Number:	7	

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### Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Zhihua Liu	0.00
<b>FTE Equivalent:</b>	<b>0.00</b>
<b>Total Number:</b>	<b>1</b>

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### Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Greg M. Swain	0.00	
Tim Grotjohn	0.00	
Remi Beaulac	0.00	
Tom Hamann	0.00	
<b>FTE Equivalent:</b>	<b>0.00</b>	
<b>Total Number:</b>	<b>4</b>	

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### Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Rodolfo Estrada	0.00	Chemistry
Michael Regan	0.00	Chemistry
Lexi Rogien	0.00	Computer and Electrical Engineering
<b>FTE Equivalent:</b>	<b>0.00</b>	
<b>Total Number:</b>	<b>3</b>	

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### Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: ..... 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

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### Names of Personnel receiving masters degrees

<u>NAME</u>
<b>Total Number:</b>

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### Names of personnel receiving PHDs

<u>NAME</u>
<b>Total Number:</b>

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**Names of other research staff**

NAME

PERCENT SUPPORTED

**FTE Equivalent:**

**Total Number:**

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**Sub Contractors (DD882)**

**Inventions (DD882)**

## Scientific Progress

## Executive Summary

Funds were used to purchase a Renishaw inVia Reflex Spectrometer System for Raman and Photoluminescence spectral analysis of thin film coatings, bulk materials, powders and nanoparticles. The instrument is extensively used to characterize advanced electrochemical and electronic materials. The instrument is equipped with a confocal microscope, two lasers for excitation at different wavelengths, a movable stage and optics for spatial imaging, a temperature-controlled sample compartment, and photoluminescence imaging. The instrument is used by undergraduate and graduate students as well as faculty from across the MSU campus who are engaged in the characterization and study of new and emerging materials. This Renishaw system is a powerful material characterization tool that provides exquisite morphological, elemental and electronic property (dopant distribution) information spatially across a material (surface and bulk). The instrument supports advanced interdisciplinary research (chemistry, materials science, electronics and physics) in the department and across campus, and is aiding in our understanding of new materials and molecular interfaces, interfacial electron-transfer processes, electrocatalysis, electronic properties of materials, and the physical and chemical properties of inorganic quantum dots. Several ongoing research projects are greatly benefiting from the new instrument. Some of the project accomplishments during the past year are highlighted below.

In addition to benefiting materials research, we are using the instrument in a new experimental module on material characterization for CEM 435 Advanced Analytical Chemistry/Instrumental Analysis (20-30 undergraduate students per year).

## Research Accomplishments

Greg M. Swain (Professor, Department of Chemistry). The Renishaw system was used by graduate and undergraduate students to study the physical, chemical and electronic properties of boron-doped diamond and nitrogen-containing tetrahedral amorphous carbon (ta-C:N) thin-film and boron-doped diamond and hybrid nanocarbon powder electrodes. A goal for this work is to correlate these properties with the electrochemical performance of these materials in room temperature ionic liquids (RTILs). The structure-function relationships of these carbon materials in RTILs, as they relate to capacitance and interfacial electron transfer, have not yet been thoroughly studied. ta-C:N thin-film electrodes are of interest because they possess many of the same desirable electrochemical properties as diamond (e.g., wide working potential window, low background current, relatively rapid electron-transfer kinetics for many aqueous redox systems, and weak adsorption) but can be deposited using much milder conditions. For aqueous redox systems, the interfacial electron-transfer kinetics at boron-doped diamond are controlled in a complex manner by (i) the dopant type, concentration and distribution within a film or bulk material, (ii) morphological features such as grain boundaries, and extended and point defects, (iii) the adventitious non-diamond (amorphous sp<sup>2</sup>/sp<sup>3</sup> bonded phases) carbon content, (iv) the crystallographic orientation and (v) the surface chemistry/termination. Raman mapping was used to investigate the microstructure and dopant distribution across the different films and powders.

A comprehensive study of the electronic, chemical and electrochemical properties of one of these carbon electrodes, a boron-doped diamond optically transparent electrode, was undertaken. The electrode was prepared by depositing a thin boron-doped nanocrystalline diamond layer on quartz. Diamond OTEs possess properties superior to those of a traditional OTE, like indium tin oxide (ITO). Raman mapping was used to track the microstructure and dopant distribution across the film. Bands at 1320 cm<sup>-1</sup> (diamond mode) and at 488, 1137, 1215 and 1470 cm<sup>-1</sup> (grain boundary carbon and boron states) were uniform in intensity across the film surface consistent with a uniform microstructure and doping level. AES depth profiling was used to probe the boron dopant distribution within the film with depth. Hall effect measurements were used to determine the carrier concentration (10<sup>21</sup> cm<sup>-3</sup> across the temperature range, 298-700 K) and the carrier mobility (0.2 cm<sup>2</sup>/Vs). UV/Vis spectroscopy was used to evaluate the optical transparency of the material (typically 60% in the 300-600 nm window). The optical properties in this wavelength range are largely controlled by reflectivity losses due to the relatively high refractive index of diamond. Finally, capacitance-potential measurements and cyclic voltammetry were used to study the activity of these electrodes and their response toward a variety of redox systems in an aqueous electrolyte. Comparison capacitance measurements were made in [BMIM][BF<sub>4</sub>] and [EMIM][BF<sub>4</sub>]. The capacitance at different potentials was greater in aqueous electrolyte than in the two ionic liquids consistent with differences in the dielectric constants and sizes of the ions. The activity of the diamond OTE toward a variety of redox systems was high with heterogeneous electron-transfer rate constants of ca. 10<sup>-2</sup> cm/s. (submitted to ACS Appl. Mater. Interfaces (special issue))

Greg M. Swain. The Renishaw system was used by graduate and undergraduate students to study the chemical structure of pretreatment conversion coatings on light-weight aluminum alloys. One objective of this project is to learn how the coating structure correlates with the corrosion inhibition observed during different accelerated degradation tests. Aluminum alloys used in aerospace applications are deployed with a multi-component coating system that and primers includes a pretreatment conversion coating, a primer and a topcoat. Our focus in this project is on the structure and performance of new, non-chromate pretreatment conversion coatings. Historically, chromate (Cr(VI)-containing) conversion pretreatment coatings and primers have been used in the industry due to the passivation, adhesion and self-healing they provide. Unfortunately, Cr(VI) is highly toxic and waste solutions containing it are expensive to treat and dispose of. There is a current drive world-wide to replace chromate conversion coatings and primers with more environmentally-friendly, non-chromated coatings. The Trivalent Chromium Process (TCP) coating, originally developed by NAVAIR, is one alternate. The core components of the bath are K<sub>2</sub>ZrF<sub>6</sub>, Cr<sub>2</sub>



(SO<sub>4</sub>)<sub>3</sub> (≤5 wt%) and F-. Note that these coating baths contain Cr(III) but not Cr(VI). There are several commercial TCP coatings available, which have the same general composition, but utilize different chemicals. Therefore, there is a need to understand the structure of these coatings on different aluminum alloys and the mechanisms by which they provide corrosion inhibition. Two key questions are, is the physical and chemical structure of the coating dependent on the alloy type, and do the different coatings perform equally as well in different accelerated degradation tests?

While there is only Cr(III) in the coating bath, preliminary Raman data indicate that Cr(VI) species (CrO<sub>4</sub><sup>2-</sup>, 840-904 cm<sup>-1</sup>) can transiently form in the coating from the incorporated Cr(III) species (Cr(OH)<sub>3</sub>, 530-580 cm<sup>-1</sup>). The Cr(VI) are isolated across the coating but appear to be localized near Cu-rich intermetallic phases of the alloy. This transient formation of Cr(VI) has been observed for several of the commercial TCP coatings studied so far. Research has shown that Cr(VI) forms transiently in the TCP coating (Alodine T5900) on AA2024, 6061 and 7075 during exposure to humidified air or full solution immersion (air saturated). The Raman system has helped to establish that the formation of Cr(VI) species, which itself is a key finding, may be critical to the mechanism by which TCP coatings provide corrosion inhibition, in much the same way it does in traditional chromate conversion coatings. It is hypothesized that dissolved oxygen is locally reduced at intermetallic sites to hydrogen peroxide. The peroxide then diffuses to nearby Cr(III) sites in the coating and oxidizes them to Cr(VI). The Cr(VI) species produced are presumably labile and can diffuse to nearby corroding sites to react and provide passivation. (One manuscript is in preparation).

A graduate student and undergraduate student have also used the Raman system in a project focused on studying the microstructure and chemical composition of different TCP commercial coatings on aluminum alloys specimens before and after being subjected to beach exposure at the Kennedy Space Center. The work is not yet complete but the preliminary Raman data have shown unequivocally that Cr(VI) species (840-904 cm<sup>-1</sup>) form transiently in isolated regions across the coating during this accelerated degradation test.

Tim Grotjohn (Professor, Department of Computer and Electrical Engineering). Students and staff scientists at the Fraunhofer Center for Coatings and Diamond Technology – MSU have used the Raman system extensively to characterize single crystal diamond specimens grown for application in electronic devices. Determining the crystalline quality of single crystal diamond (SCD) is crucial in order to optimize the growth process. The most common impurity incorporated during synthesis is nitrogen. Nitrogen results in an overall yellow/brown coloration of the crystal, which is undesired for optical applications. Additionally specific defect centers containing nitrogen are introduced, most commonly the nitrogen-vacancy (NV) defect. Spintronics is an emerging field of research interest. Research is focused on using high quality diamond as material in this application. The goal is to manipulate these NV defect states. The diamond NV centers have two significant advantages: (1) they emit visible light and (2) the excitation lifetime is in the microsecond time domain. Photoluminescence imaging is the right tool for both rating the SCD quality and to map defects. Photoluminescence (PL) was carried out using the UV laser for excitation and emission in the visible spectral region was recorded. A typical PL spectrum of diamond consists of the luminescence background and the NV features. The luminescence background intensity is related to the nitrogen content. Normalizing the spectra allows for determination of the nitrogen incorporation ratio. The presence of the NV<sub>0</sub> center at 575 nm and the NV<sup>-</sup> center at 637 nm were observed in preliminary PL measurements at room temperature. The recorded PL spectra looked exactly as expected. No in-depth analysis of the spectra was yet performed to determine the nitrogen concentration. Future experiments will involve making PL measurements on diamond materials grown under different pressures up to 400 Torr. The grown materials will be laser cut and polished to obtain freestanding films. PL analysis will be a key analysis tool to rate the crystalline quality based on the nitrogen concentration. Additionally the PL spectra will help identify how the nitrogen is incorporated (substitutional or in NV center) and how the growth process influences the distribution of defect states. Having extended knowledge on defect state formation is necessary in order to grow them in a controlled matter.

Graduate students and staff scientists also regularly used Raman imaging for quality control of the SCD and polycrystalline diamond (PCD) microstructure and stress state. Diamond has a very sharp 1st order Raman peak at 1332 cm<sup>-1</sup> associated with sp<sup>3</sup> bonds. The full-width-half-maximum (FWHM) is a good measure to approximate the single substitutional nitrogen incorporated. The FWHM was easily obtained using the software's fitting routine. In PCD, sp<sup>2</sup> bonded carbon can be present in the grain boundaries. This impurity causes two significant bands: (1) the D-band around 1345 cm<sup>-1</sup> and (2) the G-band around 1560 cm<sup>-1</sup>. The presence and ratio of the peak intensities was used for verifying the grain size and quality of PCD. Boron doped PCD has additional features due to the boron incorporated. The shift of the peak position of the major boron feature at 1220 cm<sup>-1</sup> was used to determine the boron concentration incorporated into the film.

Remi Beaulac (Assistant Professor, Department of Chemistry). The Beaulac group is interested in understanding donor/acceptor processes involving semiconductor quantum dots (QDs), such as dipolar energy transfer, electron transfer, and spin-spin exchange interactions. In particular, they are trying to determine the role of nanomaterial surfaces in controlling the rates, and thus the efficiencies, of processes that involve the coupling of QDs to molecular species covalently bound to their surfaces. Whereas the photophysics of QDs have been studied in great depth over the last two decades, the surfaces of these nanomaterials are still poorly understood and not without a reason. QD surfaces are generally quite inhomogeneous, prone to rapid chemical fluctuations, extremely sensitive to surrounding changes, and, more often than not, spectroscopically silent. The group's approach to solving these complicated problems relies on the rational design of organic and inorganic ligands with tunable electronic structures, redox activities, and/or unpaired spin densities, which ultimately control the efficiencies of donor/acceptor processes between these species and QDs. The chemical nature of the QD surfaces is tuned by traditional

inorganic shell growth methods, giving access to a wide range of donor/acceptor couples which are then characterized with detailed optical, electrochemical, and magnetic probes, in order to refine our actual understanding of the interfacial processes in QDs.

A postdoctoral researcher in group regularly used the Raman imaging system to characterize the doping chemistry of colloidal indium nitride nanoparticles. This material shows an interesting localized surface plasmon resonance in the NIR, which is attributed to degenerate doping levels of the order of  $10^{20} \text{ cm}^{-3}$ , which are highly sensitive to sample preparation, morphology, and surface chemistry. The vibrational spectrum of InN was monitored by Raman spectroscopy, revealing a clear plasmon-phonon coupling signature that has never been investigated in the nanoscopic regime. The group is presently completing a detailed study to correlate that coupling to the doping chemistry in InN, which is not well understood at the moment.

Tom Hamann (Associate Professor, Department of Chemistry). The Hamann group is interested in addressing basic science problems associated with next-generation solar energy conversion systems. For example, one topic of current interest is the possibility of using hematite electrodes for photoelectrochemical (PEC) water splitting. Hematite is an interesting material since it has a unique combination of good visible light absorption and stability in aqueous electrolytes. The overall performance, however, is hampered by a short minority carrier (hole) collection length and slow water oxidation kinetics at the electrode surface. Graduate students in their group used the Raman system on occasion to characterize the hematite films deposited.

### **Technology Transfer**

There has been no technology transfer during the project period.

## **Final Project Report** (August 15, 2014 – August 14, 2015)

**Principal Investigator:** Greg M. Swain, Ph.D. (Department of Chemistry, Michigan State University)

**Project Title:** Purchase of a Raman and Photoluminescence Imaging System for Characterization of Advanced Electrochemical and Electronic Materials

**Proposal:** W911NF-14-10462

### **Executive Summary**

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material, (ii) morphological features such as grain boundaries, and extended and point defects, (iii) the adventitious non-diamond (amorphous  $sp^2/sp^3$  bonded phases) carbon content, (iv) the crystallographic orientation and (v) the surface chemistry/termination. Raman mapping was used to investigate the microstructure and dopant distribution across the different films and powders.

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A graduate student and undergraduate student have also used the Raman system in a project focused on studying the microstructure and chemical composition of different TCP commercial coatings on aluminum alloys specimens before and after being subjected to beach exposure at the Kennedy Space Center. The work is not yet complete but the preliminary Raman data have shown unequivocally that Cr(VI) species (840-904  $\text{cm}^{-1}$ ) form transiently in isolated regions across the coating during this accelerated degradation test.

*Tim Grotjohn (Professor, Department of Computer and Electrical Engineering).* Students and staff scientists at the Fraunhofer Center for Coatings and Diamond Technology – MSU have used the Raman system extensively to characterize single crystal diamond specimens grown for application in electronic devices. Determining the crystalline quality of single crystal diamond (SCD) is crucial in order to optimize the growth process. The most common impurity incorporated during synthesis is nitrogen. Nitrogen results in an overall yellow/brown coloration of the crystal, which is undesired for optical applications. Additionally specific defect centers containing nitrogen are introduced, most commonly the nitrogen-vacancy (NV) defect. Spintronics is an emerging field of research interest. Research is focused on using high quality diamond as material in this application. The goal is to manipulate these NV defect states. The diamond NV centers have two significant advantages: (1) they emit visible light and (2) the excitation lifetime is in the microsecond time domain. Photoluminescence imaging is the right tool for both rating the SCD quality and to map defects. Photoluminescence (PL) was carried out using the UV laser for excitation and emission in the visible spectral region was recorded. A typical PL spectrum of diamond consists of the luminescence background and the NV features. The luminescence background intensity is related to the nitrogen content. Normalizing the spectra allows for determination of the nitrogen incorporation ratio. The presence of the  $\text{NV}^0$  center at 575 nm and the  $\text{NV}^-$  center at 637 nm were observed in preliminary PL measurements at room temperature. The recorded PL spectra looked exactly as expected. No in-depth analysis of the spectra was yet performed to determine the nitrogen concentration. Future experiments will involve making PL measurements on diamond materials grown under different pressures

up to 400 Torr. The grown materials will be laser cut and polished to obtain freestanding films. PL analysis will be a key analysis tool to rate the crystalline quality based on the nitrogen concentration. Additionally the PL spectra will help identify how the nitrogen is incorporated (substitutional or in NV center) and how the growth process influences the distribution of defect states. Having extended knowledge on defect state formation is necessary in order to grow them in a controlled matter.

Graduate students and staff scientists also regularly used Raman imaging for quality control of the SCD and polycrystalline diamond (PCD) microstructure and stress state. Diamond has a very sharp 1<sup>st</sup> order Raman peak at 1332 cm<sup>-1</sup> associated with sp<sup>3</sup> bonds. The full-width-half-maximum (FWHM) is a good measure to approximate the single substitutional nitrogen incorporated. The FWHM was easily obtained using the software's fitting routine. In PCD, sp<sup>2</sup> bonded carbon can be present in the grain boundaries. This impurity causes two significant bands: (1) the D-band around 1345 cm<sup>-1</sup> and (2) the G-band around 1560 cm<sup>-1</sup>. The presence and ratio of the peak intensities was used for verifying the grain size and quality of PCD. Boron doped PCD has additional features due to the boron incorporated. The shift of the peak position of the major boron feature at 1220 cm<sup>-1</sup> was used to determine the boron concentration incorporated into the film.

*Remi Beaulac (Assistant Professor, Department of Chemistry).* The Beaulac group is interested in understanding donor/acceptor processes involving semiconductor quantum dots (QDs), such as dipolar energy transfer, electron transfer, and spin-spin exchange interactions. In particular, they are trying to determine the role of nanomaterial surfaces in controlling the rates, and thus the efficiencies, of processes that involve the coupling of QDs to molecular species covalently bound to their surfaces. Whereas the photophysics of QDs have been studied in great depth over the last two decades, the surfaces of these nanomaterials are still poorly understood and not without a reason. QD surfaces are generally quite inhomogeneous, prone to rapid chemical fluctuations, extremely sensitive to surrounding changes, and, more often than not, spectroscopically silent. The group's approach to solving these complicated problems relies on the rational design of organic and inorganic ligands with tunable electronic structures, redox activities, and/or unpaired spin densities, which ultimately control the efficiencies of donor/acceptor processes between these species and QDs. The chemical nature of the QD surfaces is tuned by traditional inorganic shell growth methods, giving access to a wide range of donor/acceptor couples which are then characterized with detailed optical, electrochemical, and magnetic probes, in order to refine our actual understanding of the interfacial processes in QDs.

A postdoctoral researcher in group regularly used the Raman imaging system to characterize the doping chemistry of colloidal indium nitride nanoparticles. This material shows an interesting localized surface plasmon resonance in the NIR, which is attributed to degenerate doping levels of the order of 10<sup>20</sup> cm<sup>-3</sup>, which are highly sensitive to sample preparation, morphology, and surface chemistry. The vibrational spectrum of InN was monitored by Raman spectroscopy, revealing a clear plasmon-phonon coupling signature that has never been investigated in the nanoscopic regime. The group is presently completing a detailed study to correlate that coupling to the doping chemistry in InN, which is not well understood at the moment.

*Tom Hamann (Associate Professor, Department of Chemistry).* The Hamann group is interested in addressing basic science problems associated with next-generation solar energy conversion systems. For example, one topic of current interest is the possibility of using of hematite electrodes for photoelectrochemical (PEC) water splitting. Hematite is an interesting material since it has a unique combination of good visible light absorption and stability in aqueous electrolytes. The overall performance, however, is hampered by a short minority carrier (hole) collection length and slow water oxidation kinetics at the electrode surface. Graduate students in their group used the Raman system on occasion to characterize the hematite films deposited.